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(54) Cosmetic compositions containing clays and preservatives

(57) Cosmetic composition comprising:

(a) from about 0.1% to about 10% by weight of a crosslinked polymer of acrylic acid; and
(b) from about 0.1% to about 10% by weight of a nonionic surfactant having the formula $R(OCH_2CH_2)_nOH$ wherein R is a C_{10}-C_{16} alkyl group and n is a number average value in the range from about 3 to about 30;
(c) preservative; and
(d) clay;
wherein the composition has a pH of about 6 or less.

The cosmetic composition of the invention provides improved product stability and increased viscosity.

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Cosmetic Compositions

Field of the Invention

The present invention relates to cosmetic compositions, in particular to low pH cosmetic compositions comprising carbomer polymers, preservatives and clays.

Background of the Invention

Preservatives such as methyl and propyl parabens are commonly used in cosmetic compositions. The chemical name for methyl paraben is methyl p-hydroxybenzoate. It has been found however that in certain cosmetic compositions methyl and propyl parabens have a tendency to break down, leading to paraben loss in the final formulation. In particular, when methyl paraben is incorporated into cosmetic compositions with carboxylic acid derivatives, such as benzoyl peroxide, and clays, such as bentonite clay, methyl paraben degradation can occur.

Bentonite clay is a natural clay containing a high proportion of montmorillonite, a native hydrated aluminium silicate in which some aluminium and silicon atoms may be replaced by other atoms such as magnesium and iron. It is commonly used in cosmetic compositions as a gelling/swelling agent and as an oil absorbing agent. In its native state, bentonite clay is made up of individual dipolar platelets with edges having a net positive charge and faces having a net negative charge. The grade of bentonite clay commonly used in cosmetic products is "activated", resulting in a more pronounced negative charge at its surface. Activation is carried out by treating

the native clay with sodium hydroxide. This activation step enables the clay to swell or gel in aqueous environments and hence helps to build viscosity of product. While not wishing to be bound by theory it is believed that both activated and non-activated clays can cause paraben degradation, with the activated bentonite causing especially high levels of paraben degradation.

One way of overcoming the problem of paraben degradation in cosmetic compositions containing clays is to formulate the compositions at low pH in order to neutralise the surface of the clay platelets. However, at low pH conditions, clays such as bentonite tend to be less effective at providing gelling/thickening benefits. Therefore there is a need for increasing the viscosity of low pH compositions which contain such clays.

Gelling agents such as the carbomer polymers commercially available under the tradename Carbopol resins from B.F. Goodrich, Ohio, USA, are well known gelling/thickening agents for use in cosmetic compositions. Carbomers are crosslinked acrylic acid polymers. There are two mechanisms governing the performance of carbomer resins as thickening agents. The most common method is to convert the resins to appropriate salts. This is readily done with neutralizing agents such as sodium, potassium or ammonium hydroxide when water and other polar solvents are involved. For less polar or non-polar solvent systems, amines can be used for neutralization. In either case, the neutralized gelling agent expands from its coiled state to cause instantaneous gellation and thickening of the composition.

A second thickening mechanism for carbomer gelling agents is described in "Thickening Cosmetics without Neutralization"; by Walter Lang, Drugs and Cosmetics Industry, 1972, Vol 110, pages 52-54, and pages 126-128 involves the use of hydroxyl donor such as polyethoxy nonionic surfactants or polyhydroxy materials. The combination of a carboxyl donor from the carbomer polymer and one or more hydroxyl donors results in thickening due to the formation of hydrogen bonds.

It has now been found that by incorporating carbomer polymers and certain polyethoxy nonionic surfactants into low pH cosmetic compositions comprising clay, such as bentonite, and preservative, such as paraben preservative, compositions are provided which exhibit reduced preservative degradation together with significantly increased viscosity.

It is accordingly an object of the present invention to provide a cosmetic composition having a low pH which exhibits increased viscosity and product stability.

Summary of the Invention

According to the present invention there is provided a cosmetic composition comprising:

(a) from about 0.1% to about 10% by weight of a crosslinked polymeric gelling agent; and

(b) from about 0.1% to about 10% by weight of a nonionic surfactant having the formula $R(OCH_2CH_2)_nOH$ wherein R is a C_{10}-C_{16} alkyl group and n is a number average value in the range of from about 3 to about 30;

(c) preservative; and

(d) clay;

wherein the composition has a pH of about 6 or less.

The cosmetic compositions of the present invention provide increased viscosity and product stability.

All levels and ratios herein are by weight of composition unless otherwise specified.

Detailed Description of the Invention

The cosmetic compositions comprise crosslinked polymeric gelling agent, nonionic surfactant, preservative and clay and have a pH of about 6 or less. In preferred embodiments the compositions have a pH of about 5 or less, preferably of about 4 or less.

Gelling Agent

A first essential ingredient herein is a crosslinked polymeric gelling agent for forming a gel in the compositions of the present invention. The gelling agent is

generally present in the compositions herein at a level of from about 0.1% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.5% to about 3% by weight.

The gelling agents for use herein are crosslinked polymeric gelling agents. These can be obtained by the polymerisation or copolymerisation of appropriate monomers and then by crosslinking the polymers with a suitable crosslinking agent.

Suitable monomers for use in the crosslinked polymeric gelling agents include unsaturated, polymerizable carboxyl-containing monomers. Monomers for use herein can be monoethyleneically or polyethyleneically unsaturated. Suitable monomers of this type include acrylic acid, methacrylic acid, ethacrylic acid, beta-methacrylic acid (crotonic acid), cis-alpha-methylcrotonic acid (angelic acid), trans-alkpha-methyl-crotonic acid (tiplic acid), alpha-butylcrotonic acid, alpha-phenylacrylic acid, alpha-benzylacrylic acid, alpha-cyclohexylacrylic acid, beta-phenylacrylic acid (cinnamic acid), coumaric acid (ortho-hydrocinnamic acid), umbellic acid (p-hydroxycoumaric acid) and the like. Mixtures of these monomers can also be used. Reference to any of the monomer "acids" is intended to include the corresponding monomers in salt form.

Also suitable for use herein are hydrophobically-modified carboxylate monomers, such as C1-C30 alkyl substituted carboxylate-containing monomers, such as C1-C30 acrylic acid (acrylate) monomers. These can be used to form hydrophobically modified, cross-linked copolymers wherein the modified polymers have amphipathic properties. Mixtures of these monomers can also be used.

Preferred monomers for use herein are carboxyl-containing monoethyleneically unsaturated monomers, especially acrylic acid and hydrophobically modified carboxylate monomers, especially C1-C30 alkyl substituted acrylate monomers, and mixtures thereof.

Copolymers prepared from one or more of the above monomers together with one or more other monomers can also be used as long as the resulting copolymers are safe and effective for use as gelling agents in the compositions herein. Examples of other monomers include, but are not limited to spacer monomers such as vinyl pyrrolidone, vinyl acetate, vinyl propionate, and the like.

Suitable crosslinking agents for use herein include non-polyalkenyl polyether difunctional crosslinking agents, polyalkenyl polyether crosslinking agents and diolefinic non-hydrophilic macromeric crosslinking agents.

Suitable non-polyalkenyl polyether difunctional crosslinking agents include divinyl glycol, 2,3-dihydroxyhexa-1,5,-diene, 2,5-dimethyl-1,5-hexadiene, divinylbenzene, N,N-diallylacrylamide, N,N-diallylmethacrylamide and the like. Suitable polyalkenyl polyether crosslinking agents include those containing two or more alkenyl ether groupings having terminal H2C=C< groups, prepared by etherifying a polyhydric alcohol containing at least four carbon atoms and at least three hydroxyl groups with an alkenyl halide such as allyl bromide or the like, e.g. polyallyl sucrose, polyallyl pentaerythritol, or the like. Suitable diolefinic non-hydrophilic macromeric crosslinking agents include those having molecular weights of from about 400 to about 8,000 such as insoluble di- and polyacrylates and methacrylates of diols and polyols, diisocyanate-hydroxyalkyl acrylate or methacrylate reaction products, and reaction products of isocyanate terminated prepolymers derived from polyester diols, polyether diols or polysiloxane diols with hydroxyalkylmethacrylates, and the like.

The crosslinking agent is generally present at a level in the range of from about 0.05% to about 5%, preferably from about 0.1% to about 5%, especially from about 0.75% to about 2% by weight of the polymer.

Preferred gelling agents for use herein are polyalkenyl polyether-crosslinked polymers of carboxyl-containing monethyleneically unsaturated monomers and hydrophobically modified carboxyl-containing monoethyleneically unsaturated monomers. More preferred gelling agents for use herein are polyalkenyl polyether-crosslinked polymers of acrylic acid and C1-C30 alkyl substituted acrylic acid. Especially preferred gelling agents for use herein are polyallyl sucrose or polyallyl pentaerythritol-crosslinked polymers of acrylic acid and C1-C30 alkyl substituted acrylic acid. Examples of such polymers include those commercially available under the tradename Carbopol, such as Carbopol 1342 and Carbopol 2020 ETD, manufactured by B.F.Goodrich Chemical Company, U.S.A and Pemulen TR-1 (CTFA Designation: Acrylates/C10-30 Alkyl Acrylate Crosspolymer). A preferred gelling agent for use herein is Carbopol 2020 ETD.

Other suitable gelling agents for use herein are polyalkenyl polyether-crosslinked polymers of carboxyl-containing monoethyleneically unsaturated monomers, such as polyallyl

sucrose or polyallyl pentaerythritol-crosslinked polymers of acrylic acid. Examples of such polymers include those commercially available under the tradename Carbopol, such as Carbopol 934, 934P, 940, 941, 974P, 980, 981, manufactured by B.F.Goodrich Chemical Company, U.S.A.

Nonionic Surfactant

The compositions of the present invention comprise from about 0.1% to about 10%, preferably from about 0.5% to about 5%, especially from about 0.5% to about 3% by weight of nonionic surfactant having the formula $R(OCH_2CH_2)_nOH$ wherein R is a C_{10}-C_{18} alkyl group and n is a number average value in the range from about 3 to about 30. The nonionic surfactant has been surprisingly found to be valuable in combination with the other components of the compositions herein from the viewpoint of helping to reduce preservative degradation and increase product viscosity.

Examples of suitable nonionic surfactants for use herein include laureth-3, laureth-4, laureth-5, laureth-6, laureth-7 and laureth-8, deceth-8, deceth-4, deceth-6, ceteth-3, ceteth-4, ceteth-5 and ceteth-6. In preferred embodiments, the nonionic surfactant has the formula , $R(OCH_2CH_2)_nOH$ wherein R is C_{10}-C_{16} and n is a number average value in the range from about 3 to about 10. Especially preferred for use in the compositions herein from the viewpoint of increasing product stability and viscosity is laureth-8.

Preservative

The compositions of the present invention further comprise a preservative. Preservatives for which the benefits of the compositions herein can be obtained include those susceptible to degradation when used in combination with clays, such as bentonite, and carboxylic acid derivatives, such as benzoyl peroxide, such as hydroxy substituted benzoic acid esters, and in particular include paraben preservatives. The paraben preservative used herein is preferably selected from alkyl parabens such as methyl paraben, propyl paraben, ethyl paraben and butyl paraben, and mixtures thereof, most preferably methyl paraben and propyl paraben. The total level of preservative used herein is preferably from about 0.001% to about 5%, more preferably from about 0.01% to about 2%, and especially from about 0.01% to about 0.8% by weight of composition.

Clay

The compositions of the present invention further comprise one or more clays. Suitable clays for use herein include any clay suitable for use as thickeners in a cosmetic composition. The clay used herein can be activated or non-activated. The invention herein is particularly valuable for reducing the significant paraben degradation resulting from the use of activated clays.

A suitable class of clays for use herein is a smectite clay. The term "smectite clay" as used herein refers to a general class of water-insoluble silica or silicate mineral clays. Suitable smectite clays for use herein are those smectite clays having a swelling power with water (2g in 100ml water) of about 5ml or greater. The following test method can be used to determine the swelling power with water of a particular smectite clay.

Test Method - Swelling Power with Water

2g of the smectite clay is added in twenty portions to 100ml of a 1 per cent m/V solution of sodium lauryl sulphate in a 200ml graduated cylinder about 30mm in diameter. 2 minutes is allowed between additions for each portion to settle. The cylinder is allowed to stand for 2 hours. The apparent volume of the sediment is measured.

There are two distinct classes of smectite clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in the outer layers. The dioctahedral minerals are primarily trivalent metal ion- based clays and are comprised of the prototype pyrophyllite and the members of montmorillonite $(OH)_4Si_{8-y}Al_y(Al_{4-x}Mg_x)O_{20}$, nontronite $(OH)_4\ Si_{8-y}Al_y\ (Al_{4-x}Fe_x)O_{20}$ and volchonskoite $(OH)_4Si_{8-y}Al_y\ (Al_{4-x}Cr_x)O_{20}$, where x has a value of from 0 to about 4.0 and y has a value of from 0 to about 2.0.

The trioctahedral minerals are primarily divalent metal ion based and comprise the prototype talc and the members hectorite $(OH)_4Si_{8-y}Al_y(Mg_{6-x}Li_x)O_{20}$, saponite $(OH)_4(Si_{8-y}Al_y)\ (Mg_{6-x}Al_x)O_{20}$, sauconite $(OH)_4Si_{8-y}Al_y(Zn_{6-x}Al_x)O_{20}$ vermiculite $(OH)_4Si_{8-y}Al_y(Mg_{6-x}Fe_x)O_{20}$, wherein y has a value of 0 to about 2.0 and x has a value of 0 to about 6.0.

Alkali and alkaline earth metal salts of smectite clays are also intended for inclusion herein within the term smectite clay.

Examples of commercially available alkali and alkaline earth metal montmorillonites, saponites and hectorites are as follows:-

Sodium Montmorillonite
Brock
Volclay BC
Gelwhite GP
Thixo-Jel 1
Ben-A-Gel
Imvite
Sodium Hectorite
Veegum F
Laponite SP
Sodium Saponite
Barasym NAS 100
Calcium Montmorillonite
Soft Clark
Gelwhite L
Lithium Hectorite
Barasym LIH 200

The smectite clays of the type listed above generally have ion-exchange capacities of at least 50 meg/100g clay (measured for instance, as described in "The Chemistry and Physics of Clays", p.p 264-265, Interscience (1979).

Smectite-type clays as described above generally have a primary particle size of less than about 0.05μ and an external surface area greater than about 15 m^2/g, preferably greater than about 50 m^2/g. In practice however, these clays tend to exist as larger-sized agglomerates having agglomerate size of from about 1μ to about 75μ. Their moisture content is preferably adjusted to within the range from about 8% to about 20%, especially from about 10% to 15% by weight of the clay.

The smectite clay used herein is preferably selected from montmorillonite, saponite, hectorite, bentonite, and mixtures thereof, most preferably bentonite, such as that supplied by Aston Chemicals Ltd. under the tradename Gelwhite HNF. The smectite

clay is preferably present in the compositions herein at a level of from about 0.1% to about 20%, more preferably from about 1% to about 10%, especially from about 2% to about 7% by weight of composition.

Optional Ingredients

The compositions herein can comprise a wide variety of optional ingredients including the various non-limiting ingredients described below.

Acidic Skin Care Active

The compositions of the present invention preferably also comprise an acidic skin care active. Suitable acidic skin care actives for use herein are actives which are known for or can be used for anti-acne, skin desquamation, reduction of the appearance of wrinkles and fine lines, anti-aging, reduction of age spots and the like. Suitable acidic skin care actives for use herein are selected from compounds having the formula RCOR' wherein R' is selected from -OH, -OCOR", -Cl, -Br, -I, -OR", -OOH, and -NHR", and R and R" are independently selected from a substituted or unsubstituted C_1 - C_{24} alkyl or aryl group. Suitable substituents include (for example) C_1-C_{24} alkyl, C_1-C_{24} alkenyl, C_1-C_{24} alkoxy, hydroxy, oxo, nitro, amino, C_1-C_{24} aminoalkyl (e.g. aminomethyl, etc.), halo, carboxy, C_1-C_{24} alkoxyacetyl, (e.g., carboethoxy, etc.), thiol, aryl, C_3-C_{12} cycloalkyl, heteroaryl, C_3-C_{12} heterocycloalkyl (e.g., piperidinyl, morpholinyl, pyrrolidinyl, etc.), imino, thioxo, C_1-C_{24} hydroxyalkyl, aryloxy, C_1-C_{24} arylalkyl, and combinations thereof. Preferably the acidic skin care active herein is selected from C_6 aryl, especially benzoyl peroxide. Benzoyl peroxide is particularly useful herein for providing anti-acne benefits.

The compositions herein can be in the form of gels, lotions, solutions, creams, dispersions, emulsions including water-in-oil and oil-in-water emulsions, and the like. Preferably the compositions herein are in the form of emulsions or dispersions, especially oil-in-water emulsions having a low pH continuous aqueous phase and a discontinuous oil phase. Emulsions and dispersions are valuable herein for providing excellent aesthetics and excellent delivery of active ingredients to the skin. When the compositions are formulated as creams, emulsions or dispersions, the pH of the composition is the value obtained from approximately a 10% solution of the composition in water.

Oil Phase

When the compositions herein are formulated as an emulsion, the oil phase of the emulsion can comprise silicone oils, non-silicone organic oils, or mixtures thereof.

Suitable non-silicone organic oils include natural or synthetic oil selected from mineral, vegetable, and animal oils, fats and waxes, fatty acid esters, fatty alcohols, fatty acids and mixtures thereof, which ingredients are useful for achieving emollient cosmetic properties. It will be understood that the oil phase may contain, for example, up to about 25%, preferably up to only about 10% of oil phase soluble emulsifier ingredients. Such emulsifier ingredients are not to be considered as oil phase components from the viewpoint of determining the oil phase level.

Suitable organic oils for use herein include, for example, optionally hydroxy-substituted C_8-C_{50} unsaturated fatty acids and esters thereof, C_1-C_{24} esters of C_8-C_{30} saturated fatty acids such as isopropyl myristate, isopropyl palmitate, cetyl palmitate and octyldodecylmyristate (Wickenol 142), beeswax, saturated and unsaturated fatty alcohols such as behenyl alcohol and cetyl alcohol, hydrocarbons such as mineral oils, petrolatum and squalane, fatty sorbitan esters (see US-A-3988255, Seiden, issued October 26 1976), lanolin and lanolin derivatives, animal and vegetable triglycerides such as almond oil, peanut oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, shea butter, shorea butter, and sunflower seed oil and C_1-C_{24} esters of dimer and trimer acids such as diisopropyl dimerate, diisostearylmalate, diisostearyldimerate and triisostearyltrimerate. Of the above, highly preferred are the mineral oils, petrolatums, unsaturated fatty acids and esters thereof and mixtures thereof.

Suitable silicones for use herein include volatile silicones, non-volatiles silicones and mixtures thereof. The silicones are useful herein for providing skin conditioning properties. Suitable volatile silicones include cyclic and linear volatile polyorganosiloxanes.

The term "nonvolatile" as used herein shall mean the material has a vapour pressure of no more than 0.1 mm Hg at one atmosphere and 25°C. The term "volatile" as used herein shall mean materials which are not nonvolatile or which have a vapour pressure at the same conditions of more than 0.1mm Hg.

A description of various volatile silicones is found in Todd, et al.. "Volatile Silicone Fluids for Cosmetics", 91 *Cosmetics and Toiletries* 27-32 (1976).

Preferred cyclic silicones include cyclic dimethyl siloxane chains containing an average of from about 3 to about 9 silicon atoms, preferably from about 4 to about 5 silicon atoms. Preferred linear silicones include the polydimethylsiloxanes containing an average of from about 3 to about 9 silicon atoms. The linear volatile silicones generally have viscosities of less than about 5 centistokes at 25°C, while the cyclic materials have viscosities of less than about 10 centistokes. Examples of silicone oils useful in the present invention include: Dow Corning 344, Dow Corning 21330, Dow Corning 345, and Dow Corning 200 (manufactured by the Dow Corning Corporation): Silicone 7207 and Silicone 7158 (manufactured by the Union Carbide Corporation). SF:202 (manufactured by General Electric) and SWS-03314 (manufactured by Stauffer Chemical).

The nonvolatile silicones will have vapour pressures as previously defined, and preferably will have an average viscosity of from about 10 to about 100,000 cps at 25°C, more preferably from about 100 to about 10,000 cps, even more preferably from about 500 to about 6000 cps. Lower viscosity non-volatile silicone conditioning agents, however, can also be used. Viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

Suitable non-volatile silicone fluids for use herein include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polysiloxanes with amino functional substitutions, polyether siloxane copolymers, and mixtures thereof. The siloxanes useful in the present invention may be substituted and/or endcapped with any number of moieties, so long as the material remains suitable for use in a topical cosmetic product, including, for example, methyl, hydroxyl, ethylene oxide, propylene oxide, amino and carboxyl. However, other silicone fluids having skin conditioning properties may be used. The non-volatile polyalkyl siloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company as a Viscasil (RTM) series and from Dow Corning as the Dow Corning 200 series. Preferably, the viscosity ranges from about 10 $mm^2.s^{-1}$ to about 100,000 $mm^2.s^{-1}$ at 25°C. The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the

General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid. The polyether siloxane copolymer that may be used includes, for example, a polypropylene oxide modified dimethylpolysiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used.

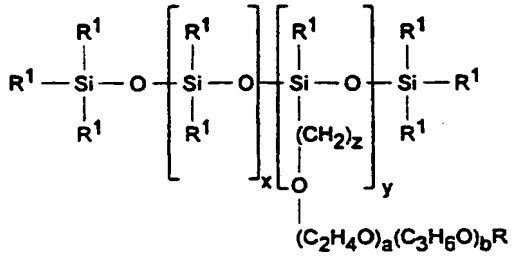
References disclosing suitable silicone fluids include US-A-2,826,551, Green; US-A-3,964,500, Drakoff, issued June 22nd, 1976; US-A-4,364,837, Pader; and GB-A-849,433, Woolston. In addition, *Silicone Compounds* distributed by Petrarch Systems Inc., 1984 provides an extensive (though not exclusive) listing of suitable silicone fluids.

Preferred non-volatile silicones for use herein include polydiorganosiloxane-polyoxyalkylene copolymers containing at least one polydiorganosiloxane segment and at least one polyoxyalkylene segment. The polydiorganosiloxane segment has the general formula:

$$R_bSiO_{(4-b)/2}$$

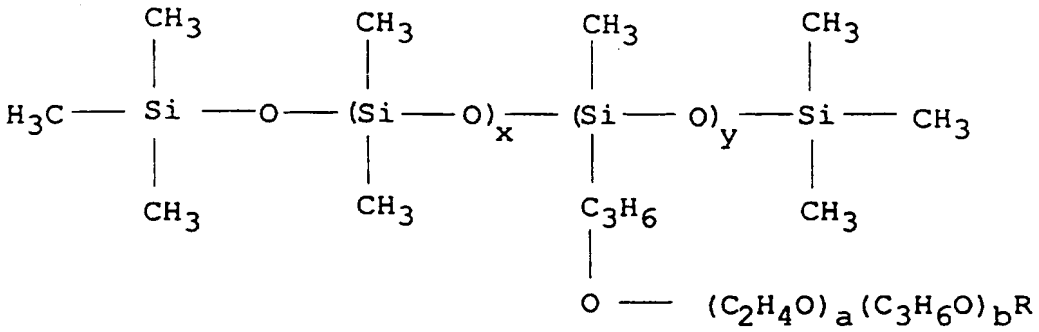
siloxane units wherein b has a value of from about 0 to about 3, inclusive, there being an average value of approximately two R radicals per silicon for all siloxane units in the copolymer, and R denotes a radical selected from methyl, ethyl, vinyl, phenyl and a divalent radical bonding said polyoxyalkylene segment to the polydiorganosiloxane segment. The polyoxyalkylene segment has an average molecular weight of at least about 500, preferably at least about 1000, and comprising from about 0 to about 50 mol percent polyoxypropylene units and from about 50 to about 100 mol percent polyoxyethylene units, at least one terminal portion of said polyoxyalkylene segment being grafted to, or covalently bonded directly or indirectly to a polydiorganosiloxane segment, any terminal portion of said polyoxyalkylene segment not bonded to said polydiorganosiloxane segment being satisfied by a terminating radical; the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in said copolymer preferably having a value of from about 2 to about 8. Such polymers are described in US-A-4,268,499.

Preferred for use herein are polydiorganosiloxane-polyoxyalkylene copolymers having the general formula:



wherein R^1 is selected from C1 to C5 alkyl groups, preferably methyl, z is in the range of from 1 to 4, x and y are selected such that the weight ratio of polydiorganosiloxane segments to polyoxalkylene segments is from about 2 to about 8, the mol ratio of a:(a+b) is from about 0.5 to about 1, and R is a chain terminating group, especially selected from hydrogen; hydroxyl; alkyl, such as methyl, ethyl, propyl, butyl, benzyl; aryl, such as phenyl; alkoxy such as methoxy, ethoxy, propoxy, butoxy; benzyloxy; aryloxy, such as phenoxy; alkenyloxy, such as vinyloxy and allyloxy; acyloxy, such as acetoxy, acryloxy and propionoxy and amino, such as dimethylamino.

More preferred for use herein are polydiorganosiloxane-polyoxyalkylene copolymers having the formula:



wherein x, y and R are as defined above.

The number of and average molecular weights of the segments in the copolymer are such that the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in the copolymer is preferably from about 2.5 to about 4.0.

Suitable copolymers are available commercially under the tradenames Belsil (RTM) from Wacker-Chemie GmbH, Geschaftsbereich S, Postfach D-8000 Munich 22 and Abil (RTM) from Th. Goldschmidt Ltd,. Tego House, Victoria Road, Ruislip, Middlesex, HA4 0YL. Particularly preferred for use herein are Belsil (RTM) 6031, Abil (RTM) B88183, DC3225C, DC5200, Abil We09 and Abil EM90. A preferred silicone herein is known by its CTFA designation as dimethicone copolyol.

The oil phase of the compositions of the present invention preferably comprises from about 5% to about 50% by weight of non-silicone organic oils. In preferred embodiments the compositions preferably comprise up to about 5%, preferably up to about 1% by weight of silicone oils.

The compositions herein may comprise an additional gelling agent including cellulose ethers (e.g. hydroxyethyl cellulose, methyl cellulose, hydroxy propylmethyl cellulose, hydroxypropyl cellulose), polyvinylpyrrolidone, polyvinylalcohol, guar gum, hydroxypropyl guar gum and xanthan gum. Such hydrophilic gelling agents are commercially available under the tradenames Klucell (RTM), Methocel (RTM) and Natrosol (RTM). A preferred hydrophilic gelling agent for use herein is Natrosol (RTM).

Other suitable low pH gelling agents which require neutralisation include Acrysol 22, Acrysol 25, Acrysol 33, Acrysol 44 (Rohm and Haas).

Suitable low pH gelling agents which do not require neutralisation include Salcare SC-91, SC-92, SC-95, SC-96, SC-97 (Allied Colloids), Sepigel 305, and Sepigel 502 (Seppic).

Other suitable materials for use in the compositions herein include glyceryl fatty esters such as glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate.

In the present compositions, humectants such as glycerine (sometimes known as glycerol or glycerin) can be present, in addition to emollient oils, at a level of from about 0.5% to about 20%, preferably from about 1% to about 10%, more preferably from about 4% to about 8% by weight of composition. Chemically, glycerine is 1,2,3- propanetriol and is a product of commerce. One large source of the material is in the manufacture of soap. Polyhydric alcohol humectants other than glycerol

which can be added herein include sorbitol, propylene glycol, butylene glycol, hexylene glycol, ethoxylated glucose and hexanetriol.

The compositions of the present invention can also comprise a water-soluble polyglycerylmethacrylate lubricant, in addition to the aforementioned polymeric gelling agent. The water soluble polyglycerylmethacrylate lubricant suitable for use herein generally has a viscosity (10% aqueous solution, 20°C, Brookfield RVT) of less than about 4000 cps, preferably less than about 1000 cps and more preferably less than about 500 cps. In addition, the polyglycerylmethacrylate lubricant preferably also has a viscosity (neat) in the range of from about 200 to about 5000 cps (Brookfield RVT, 20°C), more preferably from about 500 to about 2000 cps and especially from about 700 to about 900 cps.

The polyglycerylmethacrylate lubricants which can be used in the compositions herein are available under the trademark Lubragel (RTM) from Guardian Chemical Corporation, 230 Marcus Blvd., Hauppage, N.Y. 11787. In general, Lubragels can be described as hydrates or clathrates which are formed by the reaction of sodium glycerate with a methacrylic acid polymer. Thereafter, the hydrate or clathrate is stabilized with a small amount of propylene glycol, followed by controlled hydration of the resulting product. Lubragels are marketed in a number of grades of varying glycerate: polymer ratio and viscosity. Preferred for use herein, however, is so-called Lubragel Oil which has a typical viscosity of about 800 cps. Other suitable Lubragels include Lubragel TW, Lubragel CG and Lubragel MS.

When present, the polyglycerylmethacrylate lubricant is preferably incorporated at a level of from about 0.1% to about 10%, more preferably from about 0.2% to about 2%, and especially from about 0.3% to about 1% by weight of composition.

A number of additional water-soluble materials can be added to the compositions of the invention. Such materials include the other humectants such as sorbitol, propylene glycol, ethoxylated glucose and hexanetriol; proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives such as Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, Bromopol (2-bromo-2-nitropropane-1,3-diol) and phenoxypropanol; anti-bacterials such as Irgasan (RTM) and phenoxyethanol (preferably at levels of from 0.5% to about 5%); soluble or colloidally-soluble moisturising agents such as hyaluronic acid and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials,

Portsmith, VA, USA and described in USA-A-4,076,663; colouring agents, etc. The compositions can also contain low levels of insoluble ingredients added, for example for visual-effect purposes, e.g. thermochromic liquid crystalline materials such as the microencapsulated cholesteryl esters and chiral nematic (non-sterol) based chemicals such as the (2-methylbutyl)phenyl 4-alkyl(oxy)benzoates available from Hallcrest, Glenview, Illinois 60025, U.S.A. Water is also present at a level of from about 50% to about 99.2%, preferably from about 80% to about 95% by weight of the compositions herein. The compositions of the invention can also contain from about 0.1% to about 10%, preferably from about 1% to about 5% of a panthenol moisturiser. The panthenol moisturiser can be selected from D-panthenol ([R]-2,4-dihydroxy-N-[3-hydroxypropyl]-3,3-dimethylbutamide), DL-panthenol, calcium pantothenate, royal jelly, panthetine, pantotheine, panthenyl ethyl ether, pangamic acid, pyridoxin, pantoyl lactose and Vitamin B complex.

Other optional ingredients which can be added to the compositions of the invention include skin soothing or anti-inflammatory agents such as Allantoin and Bisabolol and antimicrobials such as Biosol, Usnic acid and Citricidal.

Other optional ingredients in the compositions herein include pigments. Suitable pigments for use herein can be inorganic and/or organic. Also included within the term pigment are materials having a low colour or lustre such as matte finishing agents, and also light scattering agents. Examples of suitable pigments are iron oxides, acylglutamate iron oxides, ultramarine blue, D&C dyes, carmine, and mixtures thereof.

The level of water used in the compositions herein is preferably from about 20% to about 90%, more preferably from about 40% to about 80%, especially from about 50% to about 80%.

The Examples below illustrate compositions which are prepared according to the process of the present invention.

Examples I-V

	I/%	II/%	III/%	IV/%	V/%
Water	----------	----------	to 100	----------	----------
Propylene Glycol	10	10	10	8.5	12.5

Benzoyl Peroxide 75%	7.5	15	14.5	10	12.5
Glyceryl Stearate	5.0	5.5	5.0	4.5	6.0
Gelwhite HNF[1]	5.0	5.5	5.0	3.9	6.4
Isopropyl Myristate	1.0	1.5	1.0	1.3	0.9
Hydrochloric Acid	1.0	0.9	1.3	1.0	1.1
Dimethicone 200 1000cst	0.2	0.15	0.3	0.13	0.4
Methyl Paraben	0.20	0.1	0.15	0.25	0.13
Propyl Paraben	0.02	0.015	0.025	0.027	0.02
Iron Oxides	0.0	0.0	0.45	0.5	0.0
Laureth-8	1.5	0.0	0.0	0.0	0.0
Laureth-3	0.0	1.5	0.0	0.0	0.0
Deceth-10	0.0	0.0	1.5	0.0	0.0
Carbopol 2020 ETD[5]	1.5	1.5	1.8	1.2	1.3
Steareth-50	0.0	0.0	0.0	1.4	0.0
Ceteth-10	0.0	0.0	0.0	0.0	1.6

1. Bentonite clay supplied by Aston Chemicals Ltd.
2. Supplied by BF Goodrich Chemical (UK) Ltd., The Lawn, 100 Lampton Road, Hounslow, Middlesex, TW3 4EB

The compositions of the above examples can be prepared as follows:

In a first vessel, the aqueous phase is prepared by adding Carbopol 2020 ETD to deionised water on stirring, and heating to 70°C. To prepare to the oil phase, isopropyl myristate, dimethicone, glyceryl monostearate and ethoxylated nonionic surfactant are mixed in a second vessel and heated to 70°C. The oil phase is then added to the aqueous phase and mixed for 5 minutes. The resulting mixture is cooled to 40°C and then homogenised at 4500 rpm during which the benzoyl peroxide and 1 molar hydrochloric acid are added. In a separate vessel the clay and propylene glycol are mixed and this premix is added to the main mix followed by homogenisation. Finally, the paraben preservatives is added whilst continuing to homogenise.

The compositions of the examples provide improved product stability and viscosity characteristics.

Claims:

1. Cosmetic composition comprising:

   (a) from about 0.1% to about 10% by weight of a crosslinked polymer of acrylic acid; and

   (b) from about 0.1% to about 10% by weight of a nonionic surfactant having the formula $R(OCH_2CH_2)_nOH$ wherein R is a C_{10}-C_{16} alkyl group and n is a number average value in the range from about 3 to about 30;

   (c) preservative; and

   (d) clay;

   wherein the composition has a pH of about 6 or less.

2. A composition according to Claim 1 comprising from about 0.1% to about 5% by weight of the crosslinked polymer of acrylic acid.

3. A composition according to Claim 1 or 2 comprising from about 0.1% to about 5% by weight of the nonionic surfactant.

4. A composition according to any of Claims 1 to 3 wherein the crosslinked acrylic acid polymer comprises form about 0.05% to about 5%, preferably from about 0.1% to about 5% by weight of polymer of a crosslinking agent.

5. A composition according to Claim 4 wherein the crosslinking agent is selected from polyallyl sucrose, polyallyl pentaerythritol or mixtures thereof.

6. A composition according to any of Claims 1 to 5 wherein n has an average value in the range of from about 3 to about 10.

7. A composition according to any of Claims 1 to 6 wherein n is a number average value of about 8 and R is lauryl.

8. A composition according to any of Claims 1 to 7 wherein the clay is selected from smectite clays having a swelling power with water (2g in 100ml water) of about 5ml or greater.

9. A composition according to Claim 8 wherein the smectite clay is selected from montmorillonite, saponite, hectorite, bentonite, and mixtures thereof.

10. A composition according to Claim 8 or 9 wherein the smectitie clay is bentonite.

11. A composition according to any of Claims 1 to 10 wherein the preservative is is an alkyl paraben preservative.

12. A composition according to Claim 11 wherein the paraben preservative is selected from methyl paraben, propyl paraben, ethyl paraben and butyl paraben, and mixtures thereof.

13. A composition according to any of Claims 1 to 12 additionally comprising from about 1% to about 20% by weight of acidic skin care active selected from compounds having the formula RCOR' wherein R is selected from a substituted or unsubstituted C_1- C_{24} alkyl or aryl group, R' is selected from -OH, -OCOR", -Cl, -Br, -I, -OR", -OOH, and -NHR", and R" is selected from a substituted or unsubstituted C_1 - C_{24} alkyl or aryl group.

13. A composition according to Claim 13 wherein the acidic skin care active is benzoyl peroxide.

14. A composition according to any of Claims 1 to 13 wherein the composition has a pH of about 5 or less, preferably of about 4 or less.

15. A composition according to any of Claims 1 to 14 wherein the composition is in the form of an emulsion, preferably an oil-in-water emulsion.

16. A composition according to any of Claims 1 to 15 comprising from about 0.1% to about 20%, preferably from about 1% to about 10% by weight of clay.

17. A composition according to any of Claims 1 to 16 comprising from about 0.001% to about 5%, preferably from about 0.01% to about 2% by weight of preservative.

The Patent Office

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Application No: GB 9614797.0 **Examiner:** John Jenkins
Claims searched: 1-17 **Date of search:** 7 October 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): A5B (BFH)

Int Cl (Ed.6): A61K 7/48

Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB 2021411 A	(SHISEIDO) See page 2 lines 14-50, Table 1, Examples 2, 4 & 12	
A	EP 0282823 A2	(KAO CORPN) See page 3 lines 10-17, 27-33 & 41, Table 2 & Example 4	
A	WPI Abstract Accession No: 82-18406E/198210 & JP 57016812 A (POLA KKKK) See abstract		

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.